

# Hydrogenation of imines catalysed by ruthenium(II) complexes based on lutidine-derived CNC pincer ligands

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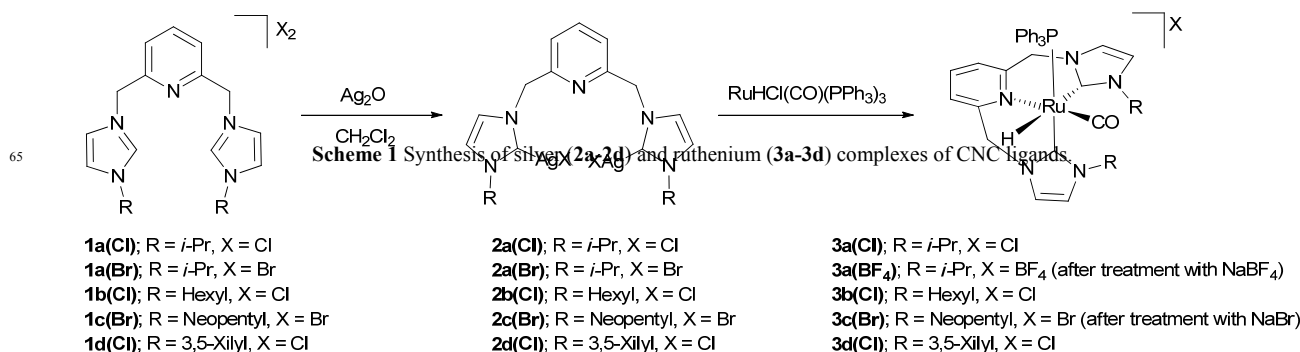
The preparation of new Ru(II) complexes incorporating *fac*-coordinated lutidine-derived CNC ligands is reported. These derivatives are selectively deprotonated by <sup>t</sup>BuOK at one of the methylene arms of the pincer, leading to catalytically active species in the hydrogenation of imines.

Lutidine-derived pincer complexes have become a prominent class of derivatives in organometallic chemistry.<sup>1</sup> In these complexes, pyridine dearomatisation occurs upon deprotonation of the acidic  $-\text{CH}_2-$  arms, leading to species that are capable of bond activation by a metal-ligand cooperative mechanism. With respect to the flanking donor groups of the pincer, attention has been largely paid to phosphorous derivatives of type PN<sub>2</sub> (P = phosphine, X = phosphine or hemilabile N-donor ligand). Of particular importance, group 8 (Ru, Fe) catalysts based on PN<sub>2</sub> ligands or their deprotonated analogues, have provided good levels of activity in the hydrogenation of a variety of polar functionalities, including ketones, esters, amides, ureas, formates, carbamates, and organic carbonates.<sup>2</sup> In addition, replacement of P-donors in PN<sub>2</sub>-Ru complexes by more electron-donating *N*-heterocyclic carbene (NHC) ligands have recently been reported. Thus, Ru pincer complexes incorporating CNN ligands with a hemilabile amine or pyridine fragment have been described.<sup>3,4</sup> Some of these derivatives are active catalysts in the hydrogenation of non-activated esters, in some cases outperforming their phosphine counterparts.<sup>3</sup> Alternatively, examples of ruthenium complexes of CNC ligands are scarce, and only derivatives of type Ru(CNC)(CO)ClH based on meridionally coordinated CNC ligands with 2,6-

diisopropylphenyl and mesityl wingtips have been reported.<sup>4</sup>

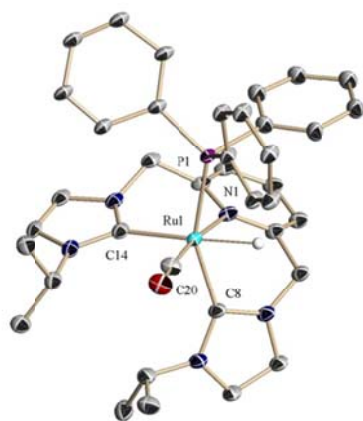
In this communication, we present the synthesis and structural characterisation of new Ru complexes **3** containing *fac*-coordinated bis-*N*-heterocyclic carbene CNC ligands. Furthermore, application of these complexes in the hydrogenation of various imines is reported.

Synthesis of new bis-imidazolium salts **1** have been effected by refluxing of acetonitrile or THF solutions of the corresponding 2,6-bis(halomethyl)pyridine and 1-substituted 1*H*-imidazole in a 1:2 ratio.<sup>5</sup> Initial experiments directed to the synthesis of ruthenium complexes incorporating CNC ligands derived from **1** were performed by reaction of the imidazolium salt **1a**(Br) with different Ru precursors (RuHCl(PPh<sub>3</sub>)<sub>3</sub>, RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>, RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub>, RuH<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>3</sub>) in the presence of base. This approach, however, leads to inseparable mixture of products, and an alternative procedure based on *N*-heterocyclic carbene transfer with Ag-NHC complexes was considered.<sup>6</sup> Reaction of bis-imidazolium salts **1** with 1 equiv of Ag<sub>2</sub>O in CH<sub>2</sub>Cl<sub>2</sub> at room temperature results in the clean formation of bimetallic silver complexes **2** (Scheme 1).<sup>5</sup> These derivatives were found adequate for CNC ligand transfer to RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub>. Thus, complexes **3a**(Cl) and **3b**(Cl) were conveniently prepared from the appropriate silver reagent **2** and RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub> in THF at 55 °C. Similarly, complexes **3a**(BF<sub>4</sub>) and **3c**(Br) were synthesised by reaction of the corresponding bromide derivatives **2a**(Br) and **2c**(Br) with RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub> followed by treatment with NaBF<sub>4</sub> and NaBr, respectively. Finally, synthesis of 3,5-xilyl-substituted **3d**(Cl) was more conveniently carried out in CH<sub>2</sub>Cl<sub>2</sub> at room temperature.



Complexes **3** have been fully characterized, and their NMR data reveal very similar features for all complexes of the series. For example, the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **3a(Cl)** shows a singlet at 42.4 ppm. Furthermore,  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra reflect the non-equivalence of the two halves of the CNC ligand. In the  $^1\text{H}$  NMR spectrum of **3a(Cl)**, the hydrido ligand gives rise to a doublet at  $-7.38$  ppm ( $J_{\text{HP}} = 30.4$  Hz), while methylene protons of the CNC ligand produce four different doublet signals in the range 4.1–5.7 ppm. The  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum shows one doublet signal for each  $\text{C}^2$  carbon atom of the NHC fragment at 180.4 ( $J_{\text{CP}} = 81$  Hz, trans to  $\text{PPh}_3$ ) and 187.9 ( $J_{\text{CP}} = 8$  Hz, trans to H), whereas the carbonyl ligand signal appears at 209 ppm as a doublet ( $J_{\text{CP}} = 15$  Hz). These data are consistent with an unprecedented *fac* coordination mode of the CNC ligand, in which one NHC fragment is placed trans to the hydrido ligand and the other is trans to  $\text{PPh}_3$ .<sup>7</sup> The CO stretch bands in the IR spectrum of complexes **3** appears in the range 1919–1934  $\text{cm}^{-1}$ .

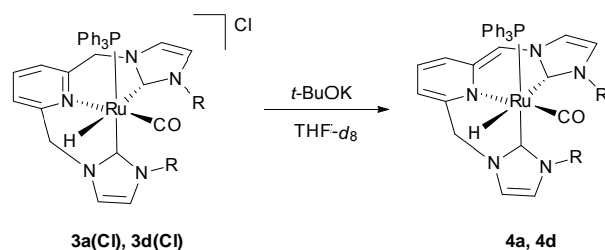
Further confirmation of the structure of coordinated CNC ligands in complexes **3** was obtained from a study by single-crystal X-ray diffraction of **3a(BF<sub>4</sub>)** (Figure 2). This complex, in the solid state, consists of a distorted octahedral structure containing the CNC pincer coordinated in a *fac* configuration ( $\text{C}^2(\text{NHC})\text{--Ru--C}^2(\text{NHC}) = 101.3(8)^\circ$ ), while the CO is placed trans to the pyridine nitrogen atom of the pincer system. Complex **3a(BF<sub>4</sub>)** is chiral by virtue of the stereogenic center present in the Ru atom. Both six-membered ruthenacycles involving the NHC and pyridine donors adopt boat-like conformations defined by dihedral angles  $\text{C}(5)\text{--N}(1)\text{--Ru}(1)\text{--C}(14)$  and  $\text{C}(1)\text{--N}(1)\text{--Ru}(1)\text{--C}(8)$  of  $25.9(15)^\circ$  and  $-47.3(15)^\circ$ , respectively. In addition,  $\text{Ru--C}^2(\text{NHC})$  distances (2.117 Å, trans to H; 2.084 Å, trans to  $\text{PPh}_3$ ) fall in the range of previously reported values,<sup>3</sup> and reflects the expected larger trans influence of the hydrido ligand.



**Fig. 2** ORTEP drawing at 30% ellipsoid probability of the cationic component of complex **3a(BF<sub>4</sub>)**. Hydrogen atoms, except for hydride ligand, have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ru(1)–N(1) 2.233(16); Ru(1)–C(8) 2.084(19); Ru(1)–C(14) 2.117(19); Ru(1)–C(20) 1.79(2); C(8)–Ru(1)–C(14) 101.3(8); N(1)–Ru(1)–C(20) 173.3(8); C(8)–Ru(1)–N(1) 80.8(7); C(14)–Ru(1)–N(1) 87.7(7); C(8)–Ru(1)–C(20) 92.6(9); C(14)–Ru(1)–C(20) 94.9(9); N(1)–Ru(1)–P(1) 92.1(4).

Treatment of complexes **3a(Cl)** and **3d(Cl)** with  $t\text{BuOK}$  in

$\text{THF-}d_8$  cleanly gives derivatives **4a** and **4d**, respectively (Scheme 2). These compounds are rather unstable and decompose in solution at room temperature in a few hours. In the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum, complex **4a** exhibits a singlet at 47.9 ppm. The hydrido ligand gives rise to a doublet at  $-7.32$  ppm ( $J_{\text{HP}} = 23.0$  Hz) in the  $^1\text{H}$  NMR spectrum, while the vinylic proton appears as a singlet at 4.77 ppm. More interestingly, the pyridine protons signals show significant upfield shifts as a consequence of pyridine dearomatisation, appearing in the range 4.6–5.5 ppm. In the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum, the carbonyl ligand produces a doublet at 210.6 ppm ( $J_{\text{CP}} = 14$  Hz), and the  $\text{C}^2\text{--NHC}$  carbon atoms appear as doublets at 181.2 ppm ( $J_{\text{CP}} = 9$  Hz) and 187.4 ppm ( $J_{\text{CP}} = 96$  Hz). Similar spectroscopic data have been found for **4d**. These values are in accord with a facially coordinated CNC ligand. In addition, intense cross-peak signals between the vinylic proton and the  $\text{C}^2$  of the NHC fragment coordinated cis to  $\text{PPh}_3$  have been observed in the  $^1\text{H}\text{--}^{13}\text{C}$  HMBC experiment, indicative of a selective deprotonation of the methylene arm of the NHC fragment coordinated trans to the hydride.



**Scheme 2** Synthesis of **4a** and **4d**.

The catalytic behaviour of complexes **3** in the hydrogenation of imines has been examined. In the presence of  $t\text{BuOK}$ , complexes **3** catalyse the hydrogenation of *N*-benzylideneaniline under 5 bar of  $\text{H}_2$  at  $70^\circ\text{C}$  in 2-methyltetrahydrofuran, using a S/C/B ratio of 1000/1/10 (Table 1, entries 1–4). In the series, complex **3b(Cl)** leads to the more active catalyst. Next, we sought to probe the scope of the reaction, and thus various *N*-aryl and *N*-alkyl aldimines were examined. Substrates bearing electron-releasing substituents are also reduced with high activities (entry 5), whereas the presence of strongly electron-withdrawing substituents in both aryl groups significantly reduces the reactivity (entries 6 and 7). Also, a *N*-benzyl aldimine was hydrogenated more slowly than the analogous *N*-phenyl imine (entry 8). Finally, complex **3b(Cl)** also catalyses the hydrogenation of a series of *N*-aryl ketimines with high turnover frequencies, independently of the electronic characteristics of the aryl substituents (entries 9–15).

## Conclusions

In summary, new ruthenium complexes **3** incorporating neutral CNC ligands have been prepared and structurally characterised. Contrary to previously observed *mer* geometry of coordinated CNC ligands, complexes **3** exhibit a *fac* coordination mode for the pincer, what might be relevant for the design of novel chiral catalysts based on structurally similar terdentate ligands. Upon reaction with  $t\text{BuOK}$ , selective deprotonation at one of the methylene arms of the CNC ligand occurs, leading to dearomatisation of the pyridine ring. Finally, complexes **3**

provide significant levels of catalytic activity in the hydrogenation of a variety of imines. This represents, to the best of our knowledge, the first application of Ru complexes containing dearomatised lutidine-derived pincer ligands in the important hydrogenation of C=N bonds.<sup>8</sup> Investigations directed to obtain further insight into the mechanism of the imine hydrogenation, as well as the use of complexes **3** in other catalytic processes are being pursued.

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## Notes and references

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† Electronic Supplementary Information (ESI) available: Representative experimental procedures, compound characterisation, crystallographic information for **3a(BF<sub>4</sub>)** (CCDC reference 894892). See DOI: 10.1039/b000000x/

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**Table 1** Hydrogenation of imines catalysed by ruthenium complexes **3**<sup>a</sup>

Entry	Imine	Cat.	Conv. (%)	TOF (h <sup>-1</sup> )
1		<b>3a(Cl)</b>	60	100.0
2		<b>3b(Cl)</b>	100	166.7
3		<b>3c(Br)</b>	26	43.3
4		<b>3d(Cl)</b>	54	90.0
5		<b>3b(Cl)</b>	100	166.7
6			80	133.3
7			54	90.0
8 <sup>b</sup>			98	16.3
9			100	166.7
10			100	166.7
11			100	166.7
12			100	166.7
13			100	166.7
14			100	166.7
15			100	166.7

<sup>a</sup> Reaction conditions, unless otherwise noted: 5 atm H<sub>2</sub>, 70 °C, 2-methyltetrahydrofuran, S/C/B = 1000/1/10, base: <sup>t</sup>BuOK, 6 h. [S] = 1.4 M. Conversion was determined by <sup>1</sup>H NMR. TOF values as calculated from conversion. <sup>b</sup> S/C/B = 100/1/10.